UT-BATTELLE

Status of Technology for Using Cementitious Materials to Stabilize Wastes

Les Dole

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contact: dolelr@ornl.gov 865-576-4319

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

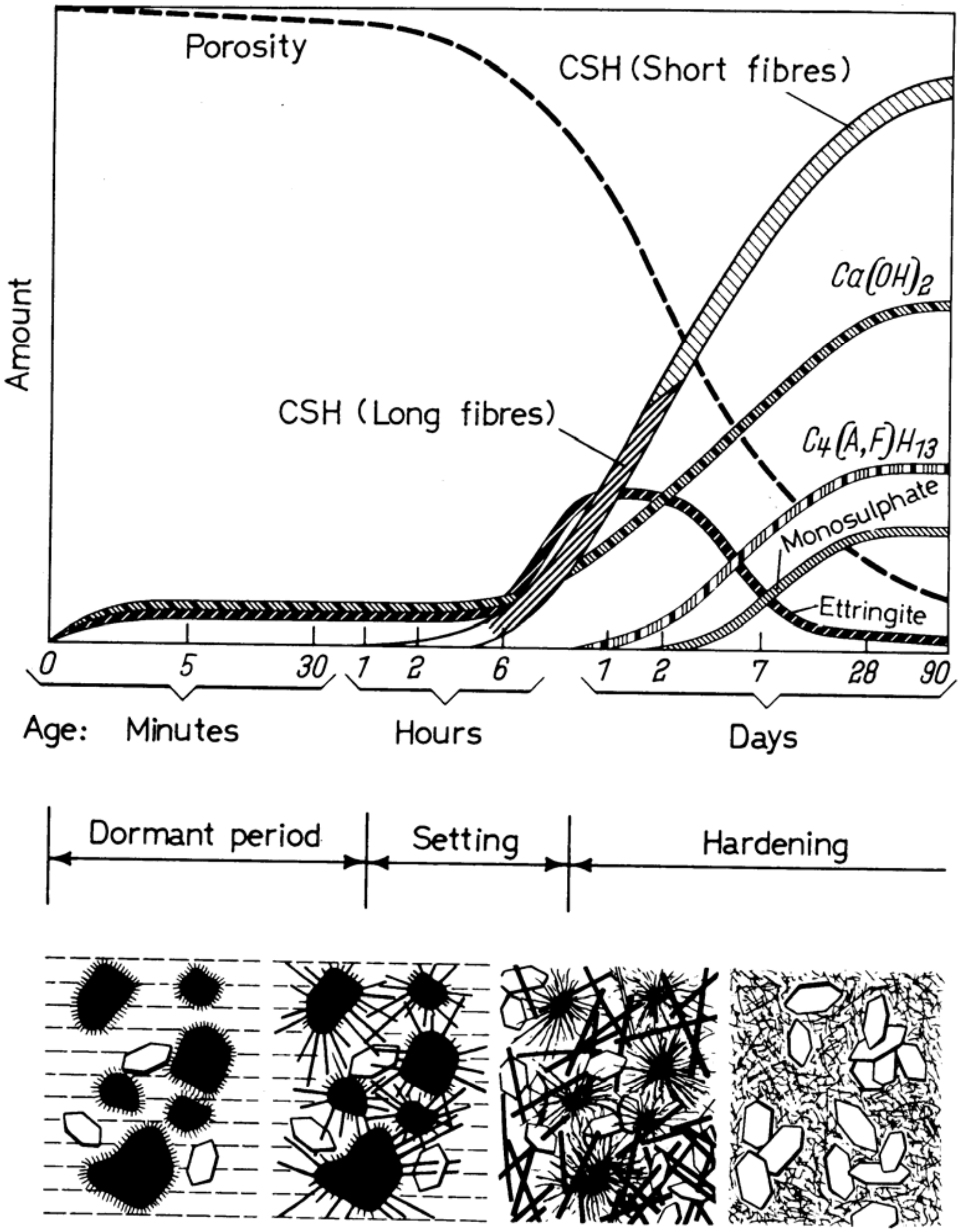
What Is a Hydraulic Cement

- Powder that reacts with water to form a "stone-like" solid

- Examples are
  - Portland cement
  - Lime silicates
  - Blast furnace slags
  - Phosphates
  - Gypsum (plaster of Paris)
  - Aluminates

- Not organic like urea-formaldehyde, polyesters, polyurethanes, thermoplastics (bitumen, polyethylene, etc.)

Reaction Sequence in Portland Cements



I. Soroka, Portland Cement Paste and Concrete, Chemical Publishing Co., 1979

What's in it and How it Reacts

- Various ranges of CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O + K_2O, TiO_2, P_2O_5, and SO_2
- Clay and limestone heated to form clinker above 1250 – 2200°C, then ground to fine powder
  - C2S, C3S, C3A, and C4AF
  - Where C= CaO, S= SiO_2, A= Al_2O_3, and F= Fe_2O_3 are 90% of the solids
- These react with water exothermally
  - 2 (CaO)3SiO2 + 7H2O(l) = 5Ca(OH)2 + CaO*2SiO2*2H2O
    ΔG35ºC = -32 kcal/mol
  - Ca(OH)2 + 2SiO2(G) + H2O = CaO*2SiO2*2H2O
    ΔG35ºC = -9 kcal/mole

Evolution of the Cement with Time

- Complex alumina-silicates with fine-textured mineral phases and large fraction of amorphous hydrosilicate phase, both of which slowly undergo diagenesis
- Matrix components leach at different rates and results in a complex series of solution reactions with groundwater adjacent to the surface with reprecipitation

Waste Constituents Influence Curing and Rheology

- **Cations**
  - **Accelerate set:**
    Ca^{++} > Ni^{++} >Ba^{++}, Mg^{++} >Fe^{+++} >Cr^{++} >Co^{++} >La^{+++} >> $NH4^{+}$, K^{+} >Li^{+} > Cs^{+} > Na^{+}
  - **Retard set:**
    Cu^{++} > Zn^{++} > Pb^{++}
- **Anions**
  - **Accelerate set:**

    OH^{-} > Cl^{-} > Br^{-} > NO_3^{-} > $SO_3^{=}$ >> $CH_3O_2^{-}$
- **Surfactants, sugars, borates, tributylphosphate, others greatly retard set**
- **Rheology controls processing and pumpability**
  - **Low ionic strength wastes use smectitc clays like bentonite, illite, and kaolinite**
  - **High ionic strength wastes use attpulgite and other needle crystalline materials and Class F fly ashes**

Material Choices to Mitigate Waste Constituents' Impacts on Waste Form Performance

- Choices of cement types
- Choices of admixtures to control waste form physical and chemical properties
  - Pozzolanic silicates
    - Reduce Ca/Si ratios
    - Reduce Al/Si ratios
    - Reduce permeability (H_2O, O_2, $SO_4^=$, Cl^-, etc.)
  - Increase internal ion exchange capacity
  - Effect reducing conditions (Eh/pH regime)

Issues with Accelerated Aging at Elevated Temperatures to Test Long-Term Durability when Reaction Paths Change

Conditions	Result
100°C for 10 minutes	Boiled egg
25°C for 28 days	Chicken
15°C for 60 days	Rotten egg

Formation Energies of Phases That Can Form in Aging Cement Pastes

Product	At 25°C	At 100°C
Hillebrandite $Ca_6Si_3O_9(OH)_6$	-2.42	-1.60
Afwillite $Ca_3Si_2O_4(OH)_6$	+3.94	+6.82
Xonotlite $Ca_6Si_6O^{17}(O_2H)$	-0.42	+0.49
Tobermorite $Ca_5Si_6O_{16}(OH)_2 \cdot 4(H2O)$	-1.38	+0.18

Anthropomorphic and Natural Analogs

- **Anthropomorphic for 2000 to 3000 years**
  - Gallo – Roman
  - Nabateans

- **Natural for over 10,000 to 1,000,000 years**
  - Million-year-old natural samples from sanidinite-facies metamorphic rocks in Marble Canyon, Texas.
  - Hatrurim formation in Israel. These formations contain many of the same phases that form in high-silica cements. For example, the minerals are natural analogs for the common cement-clinker phases "alite" (Ca_3SiO_5, C3S) and "belite" (Ca_2SiO_4, C2S).
  - Scawt Hill, Northern Ireland, occurs in a region with high precipitation.

These cementitious analogs and their alteration products provide the opportunity to study transport processes and mineral metamorphisms on geologic time scales.

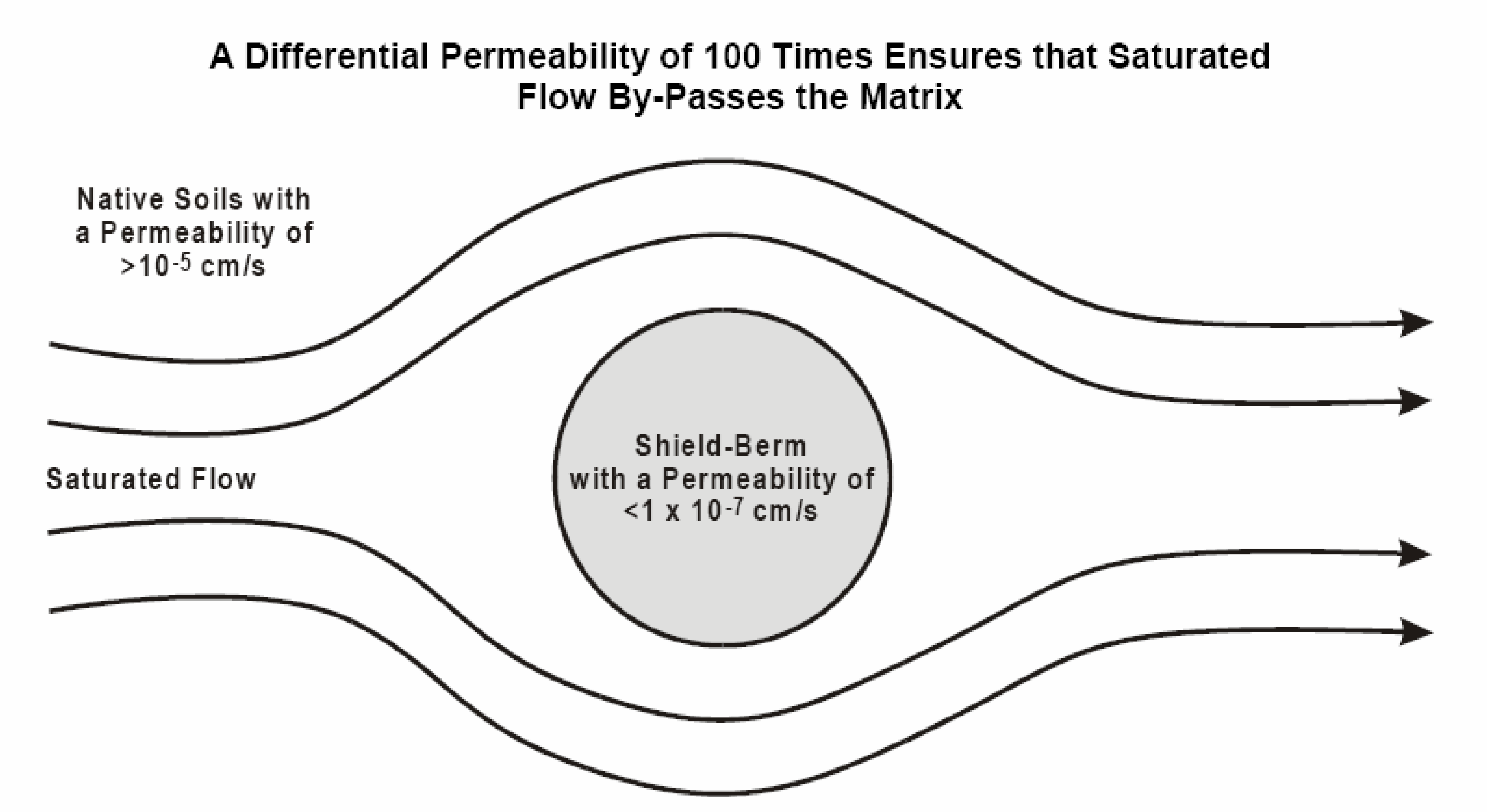
Missing Links Between Studies of Ancient Cements and Laboratory Tests

- Mass transfer coupled thermodynamic model
  - Thermodynamic data missing
  - Need for models for metastable intermediates trapped by diffusion-controlled metamorphisms
- Microprobe analytical tools to see start of phase transitions

Assessing Leach Performance at Hydraulic Extremes

- **Quasi-static flow (episodic saturation)**
  - Solubility control
  - Ion exchange equilibrium
  - Source-term = C_{sat} x Flow
- **Dynamic (monolith permeability <1/100 soil)**
  - Advection of saturated groundwater
  - Release to groundwater limited by diffusion within the monolith
  - Source-term $A_0 \{S/V\} (D_{diffusion}/\text{time})^{1/2}$

A Relatively Impermeable Monolith Has no Advection



A Not-so Practical Model for the "Effective" Diffusion Coefficient

$$K_{MB} = \left[\frac{\left(\dfrac{\text{mole of species}}{\text{mass of porous solid}} \right)}{\left(\dfrac{\text{mole of species}}{\text{volume of liquid}} \right)} \right] .$$

$$D_e = \left[\frac{D_f}{\tau^2 \cdot \left[1 + \rho_b \cdot \left[\dfrac{(1 - \epsilon)}{\epsilon} \right] \cdot K_{MB} \right]} \right] ,$$

where

τ = tortuosity, *dimensionless* (This study assumed that τ was equal to 1.47 for the compacted berm soils.)

ρ_b = bulk density of porous soil, g/cm^3

ϵ = average *effective* open porosity, *dimensionless*.

500-Year Fractional Release (FI) Model for Sr-90 Activity from Grouted GAAT Sludge from Gunite Tank W9

Effective diffusion coefficient:

$$D_e := \left(2.6\cdot 10^{-13}\right)\cdot\frac{cm^2}{sec}$$

***** Data from similar hydrofracture grouts**

** assumes most activity is Sr-90*

Time iteration

$$i := 0, 10 .. 500$$

$$t_i := i\cdot yr$$

Surface to volume:

$$\frac{S}{V} = 5.125\,cm^{-1}$$

***** Assumes entire surface on the monolith is exposed to flowing groundwater. No credit is given for the existing tank walls.**

Infinite slab diffusion model:

$$FI(t) := 2\cdot\frac{S}{V}\cdot\sqrt{\frac{D_e\cdot t}{\pi}}$$

***** calculates a conservative overestimate of release**

$$t2 := \left(0.2\cdot\frac{V}{S\cdot 2}\right)^2\cdot\left(\frac{\pi}{D_e}\right) \qquad t2 = 145.805\,yr \qquad FI(t2) = 0.2$$

****On-set of geometry specific effects***

$$t5 := \left(0.5\cdot\frac{V}{S\cdot 2}\right)^2\cdot\left(\frac{\pi}{D_e}\right) \qquad t5 = 911.278\,yr \qquad FI(t5) = 0.5$$

****Chemical half-life in monolith***

Onset of Geometric Model at FC≥0.2

Nestor, C. W., Jr., *Diffusion from Solid Cylinders*, **ORNL/SDTM-84**, Lockheed Martin Energy Research Corp., Oak Ridge National Laboratory, Oak Ridge, Tennessee, January 1980.

$$\alpha_j := \frac{\mathrm{root}(\mathrm{J0}(j), j)}{a}$$

D_e = effective diffusion coefficient, $\mathrm{cm}^2\ \mathrm{s}^{-1}$
a = cylinder radius, cm
j = j^{th} positive root of a zero-order Bessel function $[J_0(m)]$
L = cylinder half-height, cm.

Diffusion from a Cylinder:

$$\mathrm{FC}(t) := 1 - \frac{32}{\pi^2 \cdot a^2} \cdot \sum_n \sum_j \frac{e^{-\left[D_e \cdot \left[\left(\alpha_j\right)^2 + (2 \cdot n - 1)^2 \cdot \frac{\pi^2}{4 \cdot L^2}\right] \cdot t\right]}}{(2 \cdot n - 1)^2 \cdot \left(\alpha_j\right)^2}$$

$\mathrm{FC}(t2) = 0.223$ $\quad$ $\mathrm{FS}(t) := \mathrm{if}(t > t2, \mathrm{FC}(t), \mathrm{FI}(t))$ $\quad$ $F_i := \mathrm{FS}\left(t_i\right)$ $\quad$ $\mathrm{FI}_i := \mathrm{FI}\left(t_i\right)$

Example: Diffusion-Controlled Release of ^{90}Sr from a Monolith

Fraction Released

$F_{30} = 0.091$

$F_{300} = 0.303$

$F_{500} = 0.379$

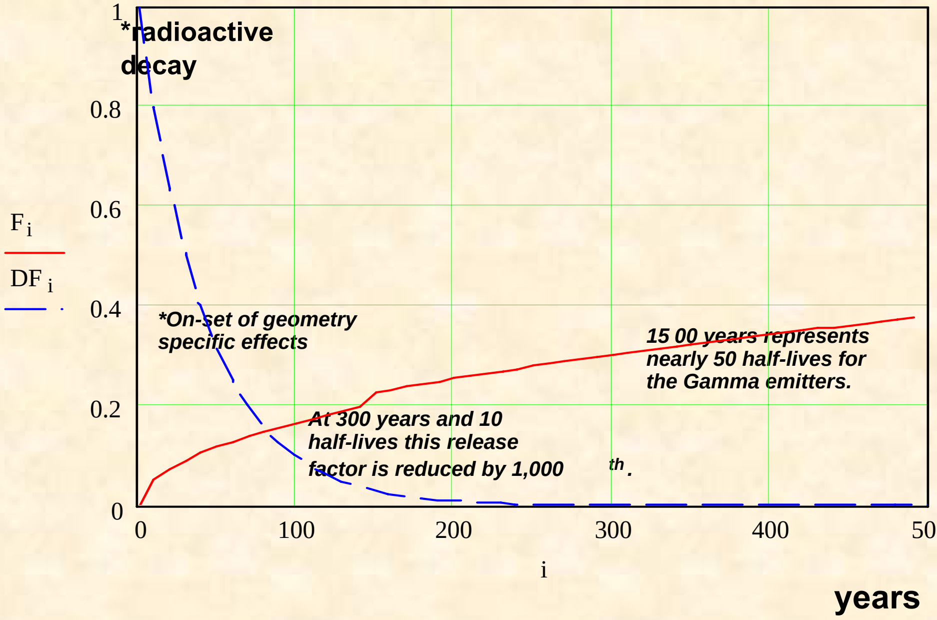
Radioactive Decay Factor

$DF_{30} = 0.5$

$DF_{300} = 9.766 \times 10^{-4}$

$DF_{500} = 9.612 \times 10^{-6}$

CURIE RELEASE FROM W9 MONOLITH as Sr-90



*radioactive decay

*On-set of geometry specific effects

At 300 years and 10 half-lives this release factor is reduced by 1,000th.

15 00 years represents nearly 50 half-lives for the Gamma emitters.

Combination of Decay and Diffusion Controlled Release

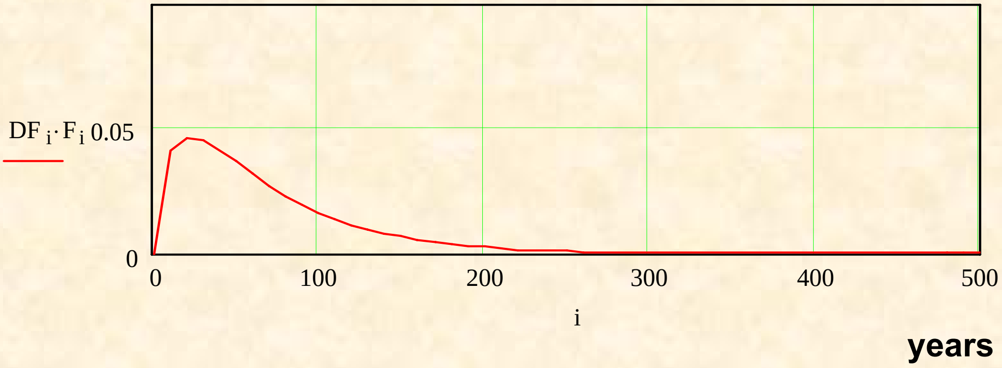
Decay Fraction X Release Fraction

$DF_{30} \cdot F_{30} = 0.045$

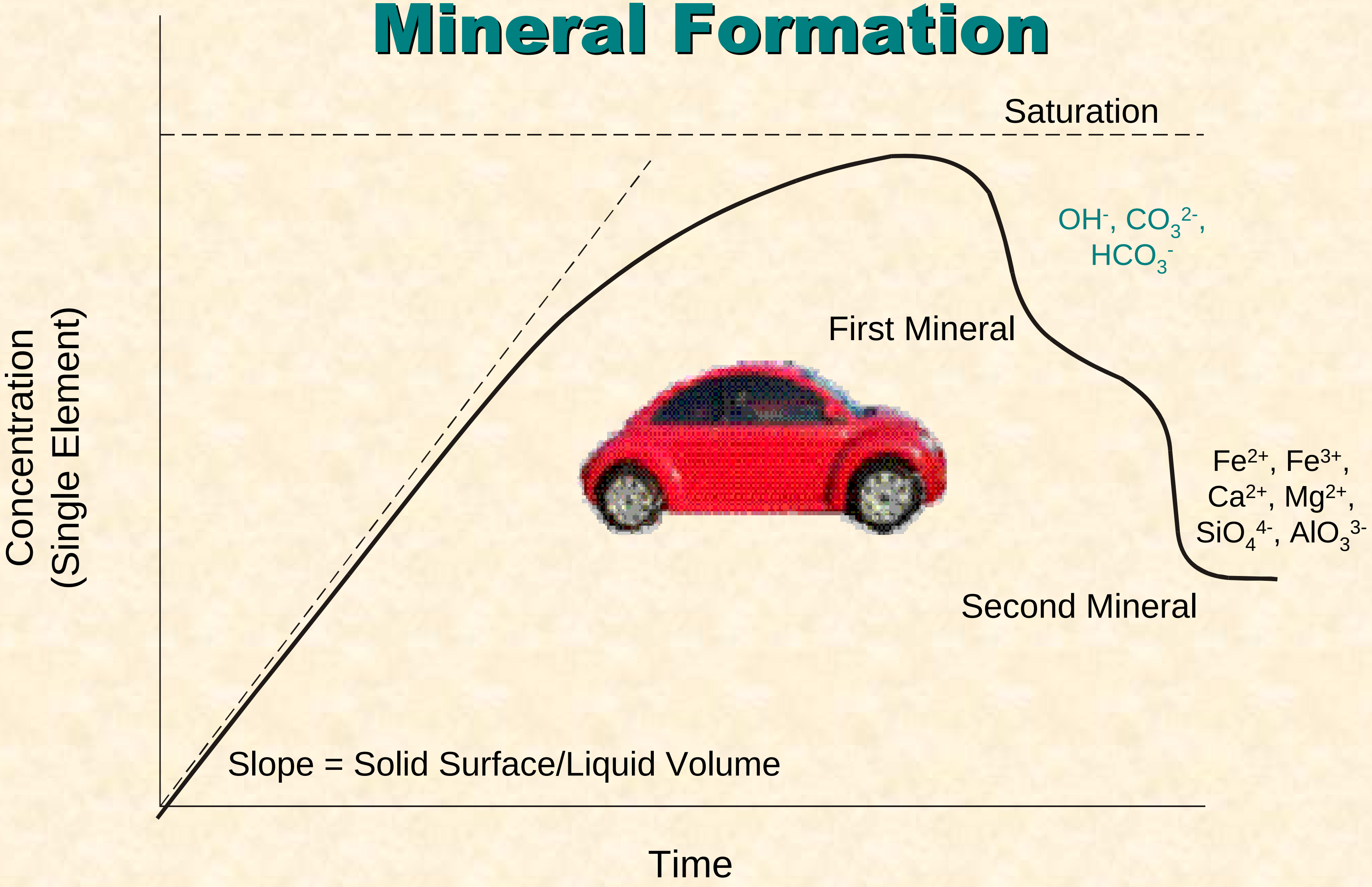
$DF_{90} \cdot F_{90} = 0.02$

$DF_{150} \cdot F_{150} = 7.047 \times 10^{-3}$

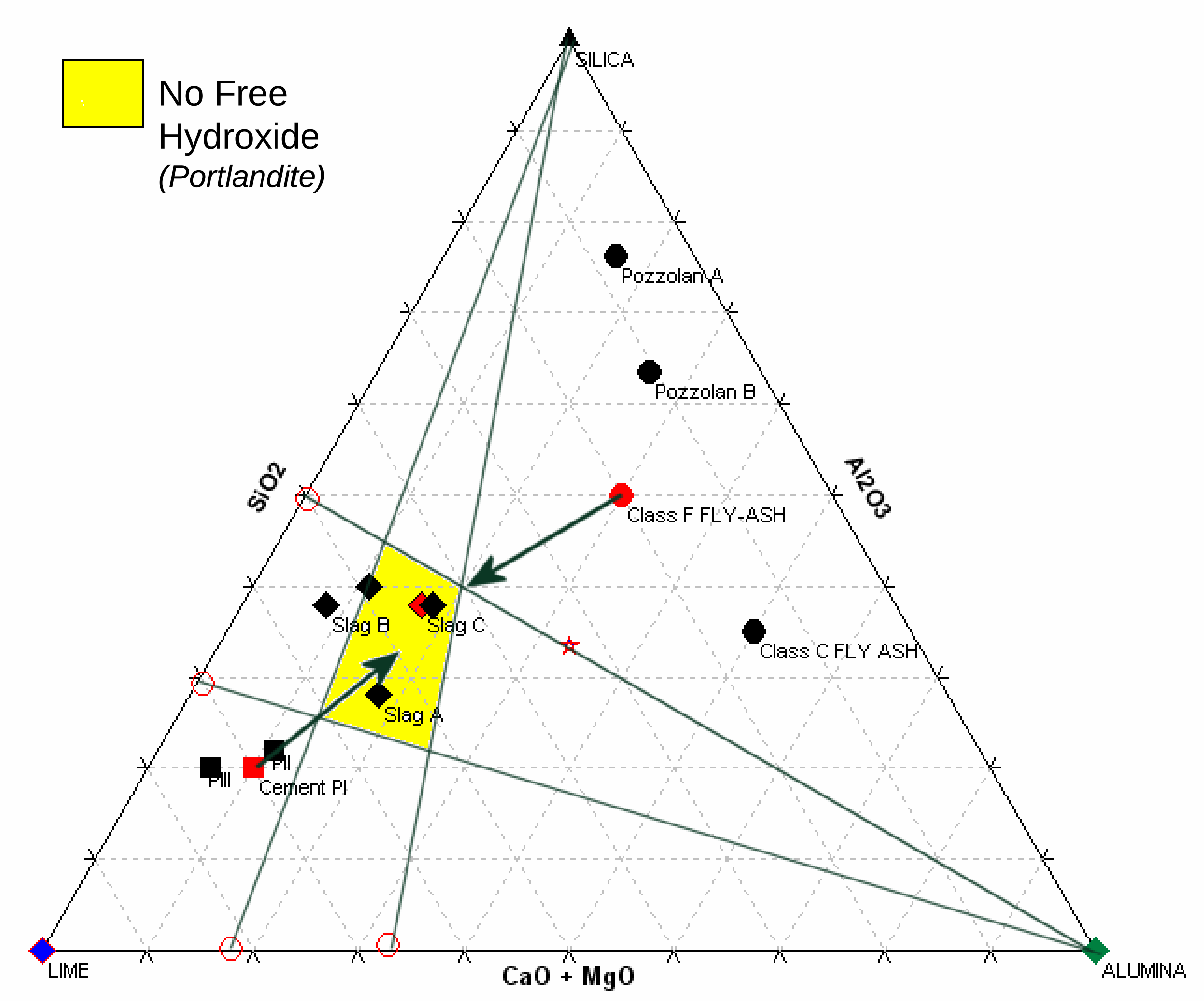
$DF_{300} \cdot F_{300} = 2.955 \times 10^{-4}$



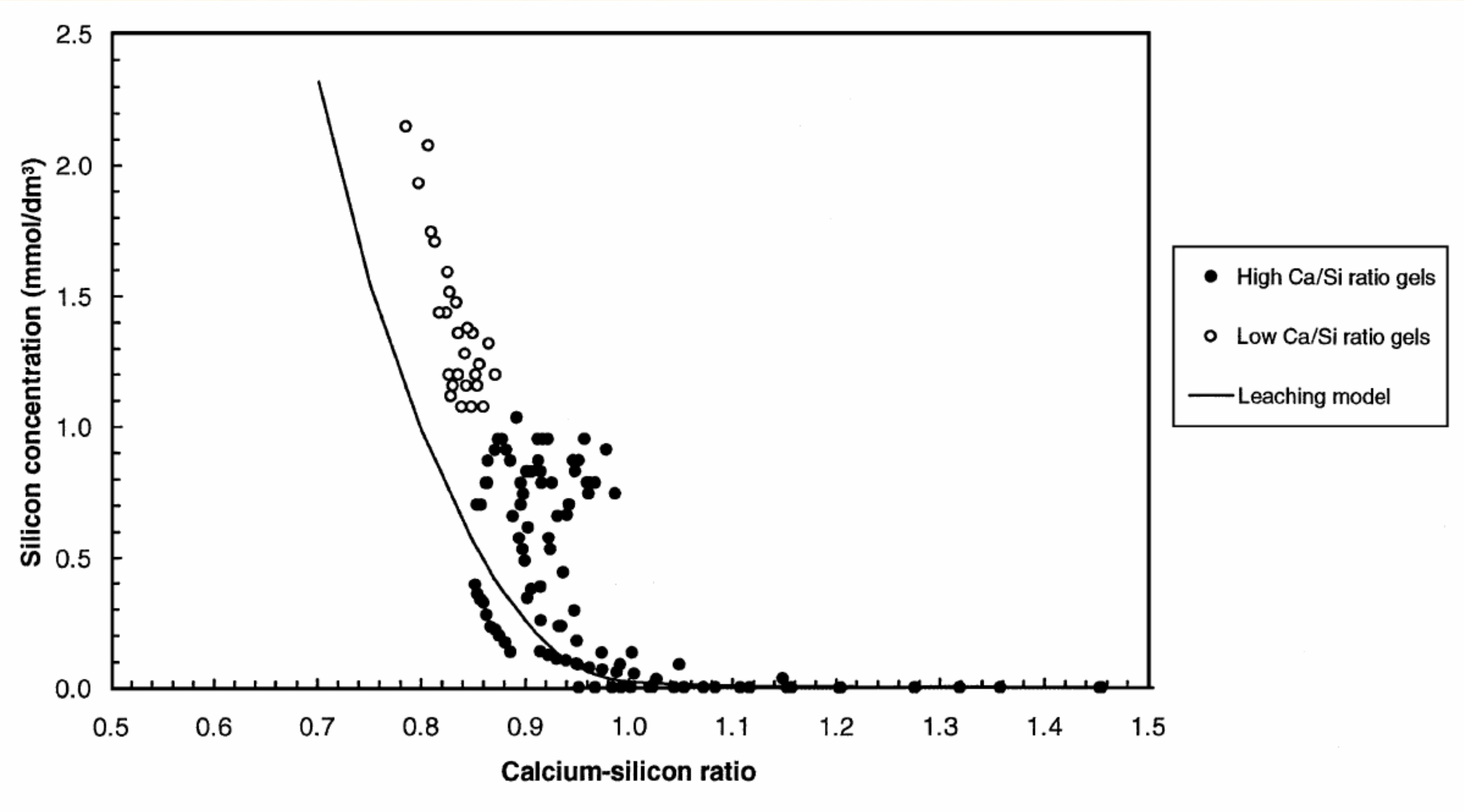
Static Leaching with Secondary Mineral Formation



Formulation of Grouts to Prevent $Ca(OH)_2$

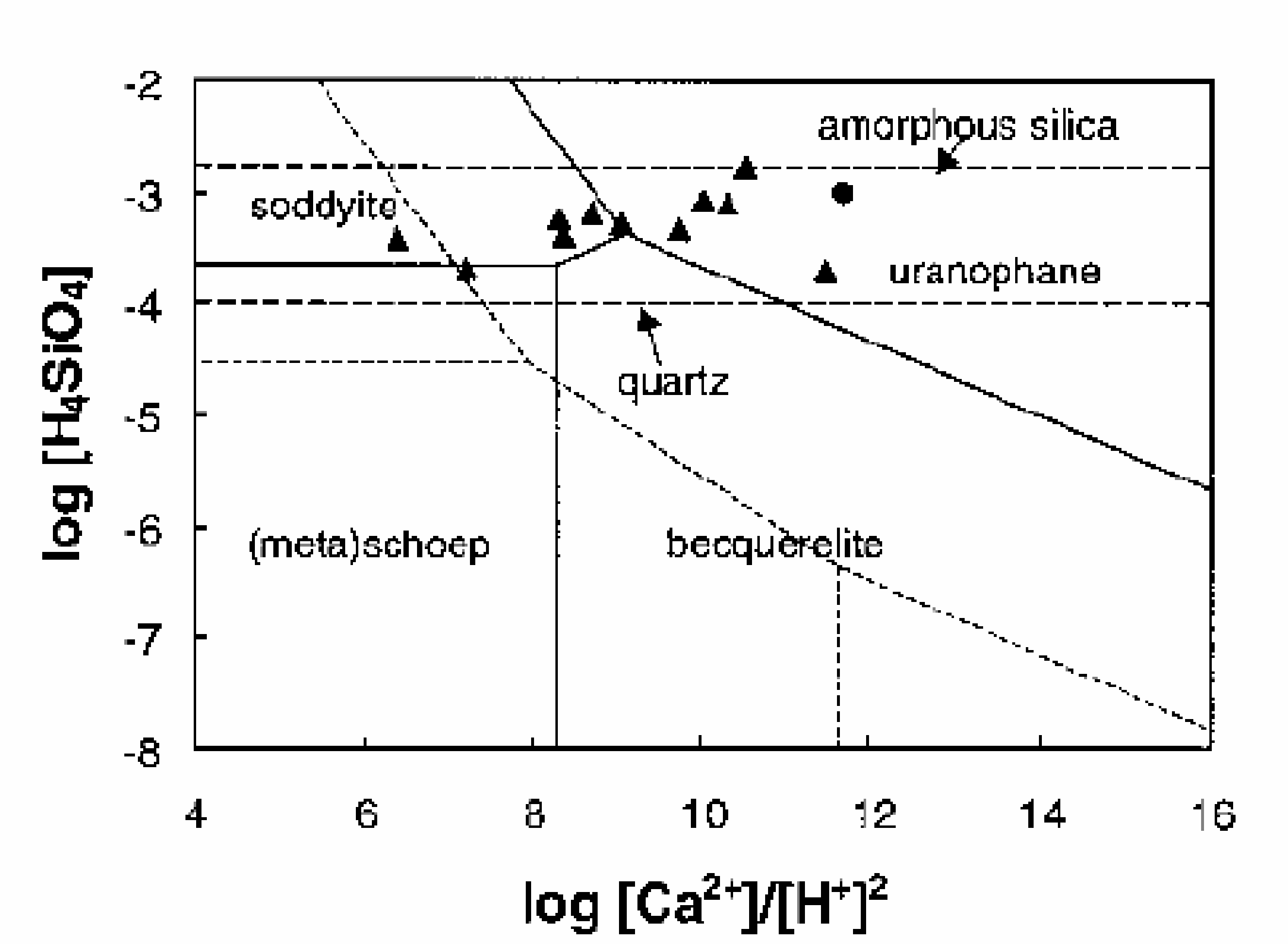


Increasing Silica in Cement Increases Silica in Leachates

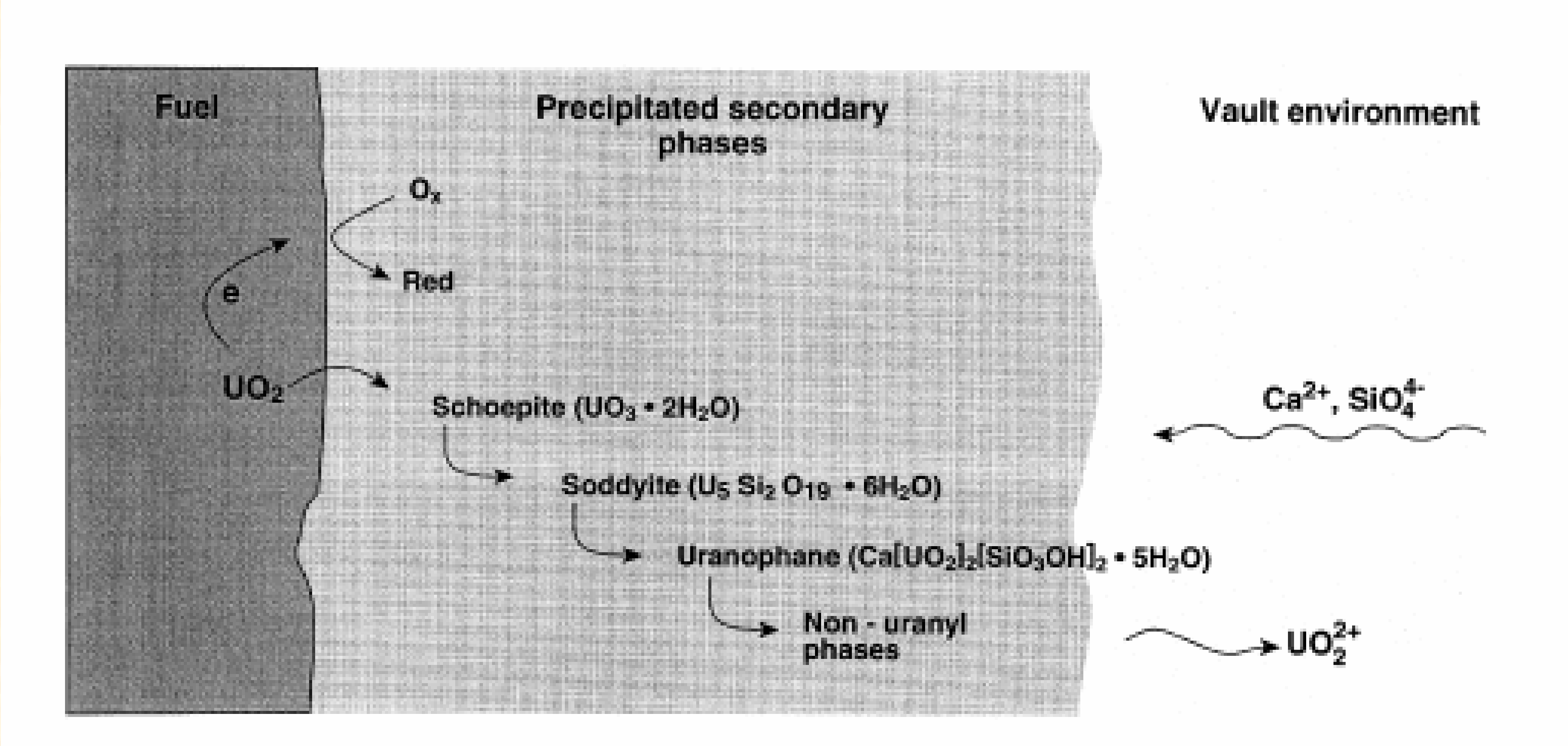


Harris, A.W., M.C. Manning, W.M. Tearle, and C.J. Tweed, Testing of models of the Dissolution of cements—leaching of synthetic CSH gels, Cement and Concrete Research, 32, pp 731–746, 2002.

High-Silica Forces Formation of Insoluble Uranium Silicates



Silicates Form a Dense Diffusion Layer on the Surface of UO_2 even under Oxidizing Conditions



Conclusions About Leach Testing

Short-term leach testing is conservative IF:

- Test does not allow for the effects of secondary minerals, which
  - Are highly selective for contaminant species
  - Forms protective diffusion surface barriers

- The monolith matrix is relatively stable in the geochemistry of the disposal horizon
  - Shares same regions of the geochemical stability fields
  - Has similar SiO_2-Al_2O_3 composition ranges

- Ultimate mechanisms of leaching, alterations, and weathering are controlled by solid-diffusion rates

General Conclusions

- There is a great body of knowledge on how to formulate cementitious waste forms to process and solidify radwastes from across the DOE complex.
- There is disagreement on how to measure and model source-terms for the leaching for nuclides into the near-field transport models.
- There is no coordinated effort to reconcile measured waste form performances with accelerated testing and natural/anthropomorphic analogs.